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Separation of cerium, light and heavy rare earth concentrates from Egyptian crude monazite

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ABSTRACT

Laboratory-scale experiments were conducted to recover cerium, light and heavy rare earth elements from Egyptian monazite in sulfuric acid medium. The method includes acid leaching of Egyptian monazite and subsequent aqueous media extraction of the leached metals into two successive stages. Rare earth double sulfate selective precipitation was carried out upon the two leach solutions to prepare concentrates containing most of the light rare earth elements. Light rare earth double sulfate concentrates were conversed to hydroxide then filtration, washing and drying at 180°C for 10 hrs were used to oxidize Ce^{3+} to Ce^{4+}. Light rare earth hydroxide cakes were leached with dilute nitric acid under pH control of 3.0 to leach most of the trivalent rare earth elements rather than Ce^{4+} which left as high cerium concentrate. The leach solution containing light and other trivalent rare earth elements was precipitated successively at pH values of 7.5, 8.5 and 9.5. Cerium concentrates contained 47 – 48% CeO and the light rare earth concentrate precipitated at pH 7.5 contained more than 64% La, Nd, Pr and Sm oxides. Solutions after the double sulfate precipitation were subjected to thorium separation at pH 1.1 then the resultant clear solution was thoroughly neutralized at pH 6.5 where the precipitate slurry was converted to hydroxide. The produced hydroxide cake was leached with HCl at pH 3.0 and the leach solution was selectively precipitated using oxalic acid to produce the first oxalate concentrate which was composed mainly from yttrium (about 18% Y_2O_3).

KEYWORDS

Crude monazite;
Leaching;
Light and heavy rare earth elements;
Thorium;
Double sulfate precipitation;
Cerium oxidation;
Trivalent rare earth;
Oxalate precipitation;
Concentrates;
Uranium.

INTRODUCTION

Rare earth elements of high purity play a significant role in many areas of contemporary techniques. They also have many scientific applications. For example, their compounds are used as catalysts in the production of petroleum and synthetic products, lanthanides are used in lamps, lasers, magnets, phosphors, motion picture projectors, and X-ray intensifying screens. Therefore, the preparation of high purity rare earth elements is very important for such technologies[1]. The extraction of lanthanide concentrates from their ores involves a number of processes, which progressively eliminate the majority of the original non-rare earth constituents of the ore. Rare earth elements can be found in a variety of minerals, but the most abundant rare earth elements are found primarily in bastnaesite and monazite. Usually monazite contains about 70% REO, and the rare earth fraction is constituted by 20 to 30% Ce_2O_3; 10 to 40% La_2O_3; significant amounts of neodymium, praseodymium, and samarium; and lesser amounts of dysprosium, erbium, and holmium. Yttrium content may vary from a trace to ~5% Y_2O_3, and thorium content of 4 to 12% is common. Some amount of uranium is also present in monazite[2].

Digestion by sulfuric acid is recommended for low grade monazite sand of different grain size in addition to the other advantages which include their availability, low cost and plant corrosion to its higher boiling point[3,4]. On the other hand, the resultant monazite sulfate solution is suitable for selective precipitation of light rare earth elements as double sulfates using anhydrous sulfate salt. The precipitate is easily filterable, washable and also convenient to store as starting material for the manufacture of rare earth materials. It can be converted to hydroxides by caustic soda. Cerous contained in rare earth hydroxides can be easily oxidized to ceric during the drying step at temperature more than 150°C which in turn unable to dissolve with dilute acids at relatively high pH[5,6].

Rare earth precipitation as oxalate is considered a better method which produces rare earth precipitate free from the undesirable sulfate, phosphate and uranium ions that interferes the latter separation processes. Rare earth oxalate precipitates are easily filterable and can readily be converted to oxides by calcinations. Completeness of oxalate precipitation was found to be virtually independent of pH between 0.4 and 3.0, and temperature between 20°C and 80°C from sulfate medium. However, pH value between 1.1 and 1.5 was preferred where the acidity can be adjusted by ammonia[7].

EXPERIMENTAL

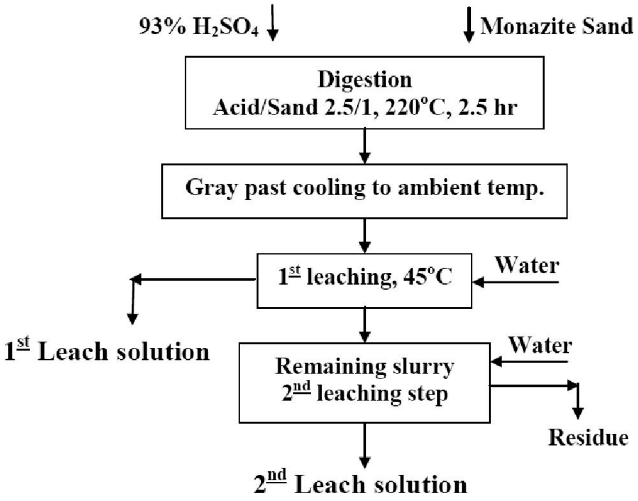
Egyptian low grade monazite was obtained as by-product during the concentration and recovery of the more abundant economic minerals e.g. magnetite, ilmenite, rutile, zircon, etc from the black sand deposits at Rosetta area on the Mediterranean coast[8]. Fifty kilograms of this low grade monazite was subjected to different procedures and treatments for preparing high grade cerium, light and heavy rare earth concentrates, taking into consideration the following initial selective separation routes[9-12]. These are summarized in the illustrated flow sheets.

Selective leaching route stages

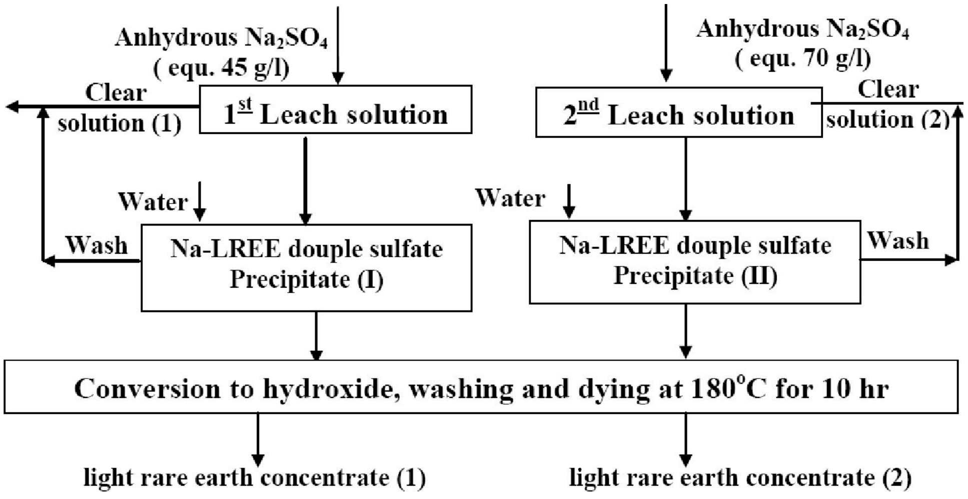
Rare earth sulfates have lower solubility at relative high temperature, where more than half of the rare earth sulfates can be left un-dissolved. Accordingly, the monazite sulfate produced after digestion can be leached with water into two successive steps. In this regard, it is beneficial to conduct the first leaching step with normal water where the heat released from excess sulfuric acid dilution increases the solution temperature to more than 45^0C. Water was added in a ratio to the monazite sand of 10 /1 and the mixture was agitated for one hour in a polypropylene tank to preserve the heat then left over night to decant. The clear solution was withdrawn, containing part of the rare earth elements with almost all of thorium and uranium. The un-leached part was thoroughly leached also with normal water in a ratio of 3.5/1 to the remaining slurry to produce the second leach step solution containing high concentration of the other rare earth elements[11].

Light rare earth elements selective separation route

Most of the light rare earth elements can be pre-



Scheme 1 : The two successive leaching steps



Scheme 2 : Steps for preparation cerium and light rare earth concentrates

cipitated selectively as double sulfates with anhydrous sodium sulfate, while most of yttrium and the other heavy rare earth elements in addition to 50 – 60% of gadolinium remain un-precipitated. Accordingly, two light rare earth concentrates were prepared through adding the Na_2SO_4 salt in concentration equivalent to 45 and 70 g/l for precipitation from the first and second leach solutions, respectively[11].

Heavy rare earth elements selective separation route

Clear solutions (1) and (2) after double sulfate precipitation were treated as follows:

(a) Thorium was firstly precipitated at pH 1.1 using 16% ammonia solution. After settling, the clear solution was withdrawn for further precipitation.

(b) The clear solution was neutralized to pH 6.5 using also 16% ammonia solution to precipitate the remained light with the heavy rare earth elements and uranium.

(c) The slurries of rare earth phosphate precipitates were converted into hydroxides using sodium hydroxide pellets (equivalent to 20%) in a poly propylene tank which kept the released heat due to the dissolution and raise the temperature of the slurry. The converted precipitates were left over night then finely washed thoroughly through re-pulping with water to free the slurry from the alkali.

(d) The produced hydroxide precipitates in slurry were leached with hydrochloric acid at control pH of 3.0. After settling, the clear solution was withdrawn leaving the residue for further leaching.

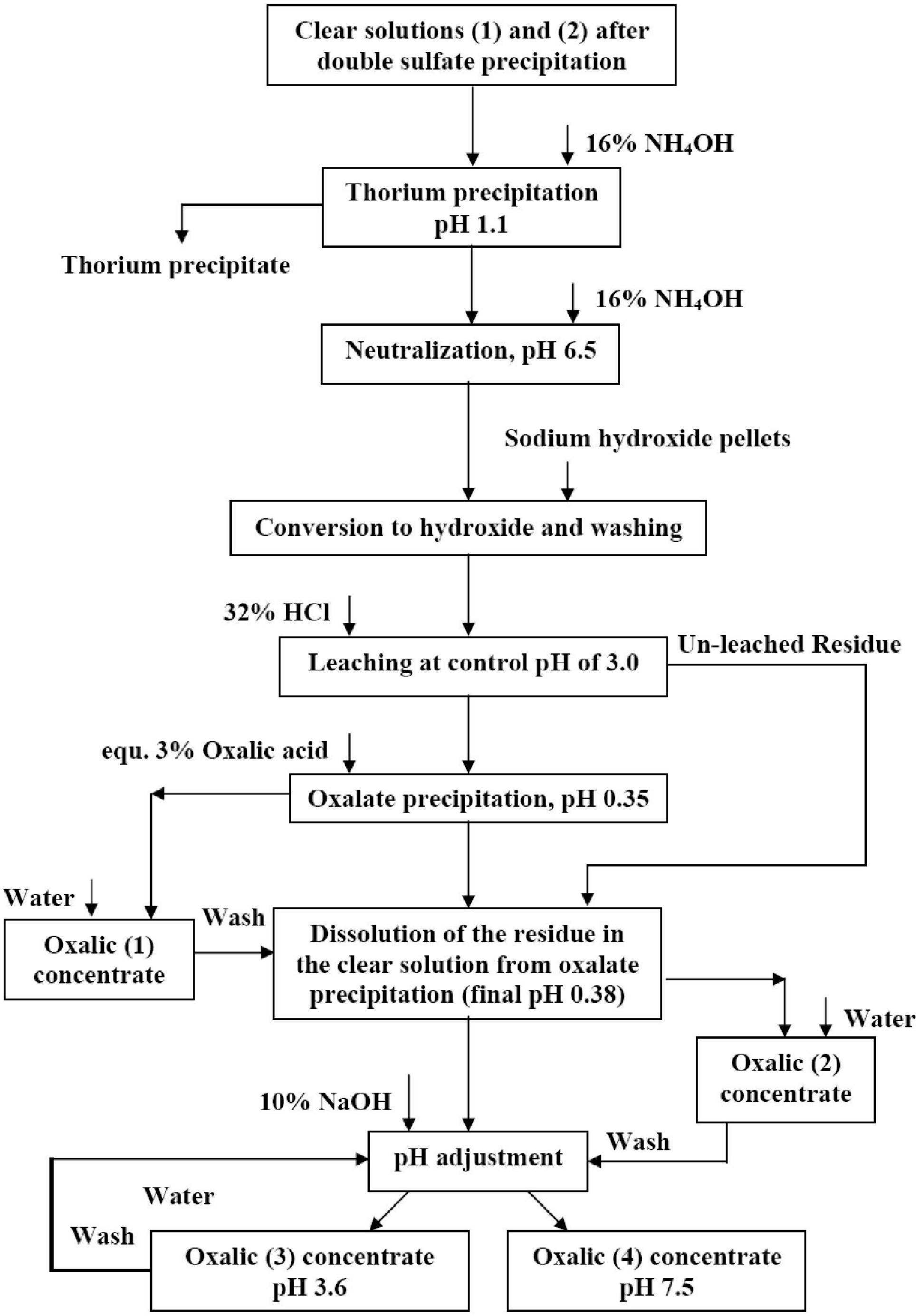
(e) The leach solutions were precipitated using oxalic acid (equivalent to 3%) where the first rare earth oxalate concentrate (denoted oxalate (1)) was produced at low pH value. The precipitate was separated after decantation and finely washed.

The clear solution from oxalate precipitation was mixed with the residue from the leaching step where another rare earth oxalate concentrate (denoted oxalate 2) was produced also at low pH value. The precipitate was separated after decantation and finely washed.

(f) The pH of the final clear solution was successively adjusted to 3.6 where another rare earth oxalate concentrate (denoted oxalate (3)) was produced. The pH 7.5 of the last precipitate was produced (denoted oxalate (4)) which contains uranium and any un-precipitated constituents.

The prepared concentrates oxalate (1) and (2) were characterized using X-ray Fluorescence Spectrometer, Bruker Pioneer S4, while the concentrates oxalate (3) and (4) were analyzed qualitatively using Scanning Electron Microscope (ESEM) operating conditions with low vacuum, 30 KV, Take-off:35.00, AmpT:25.6, Detector Type :SUTW-Sapphire, and Resolution :132.38.

Cerium selective separation route



Scheme 3 : Steps for preparation heavy rare earth concentrates

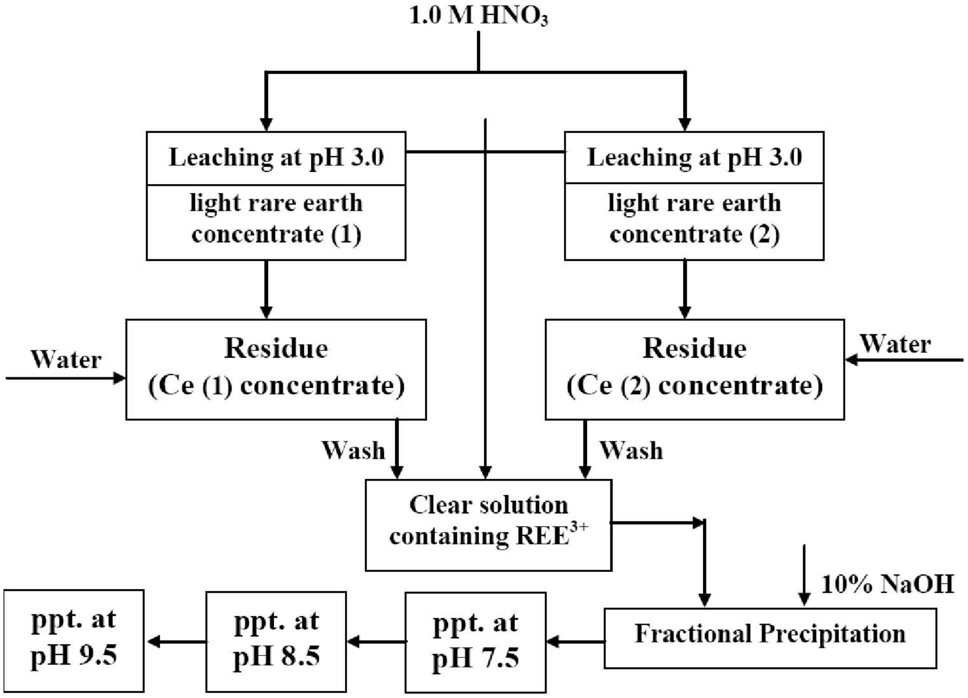
Light rare earth double sulfate concentrate was subjected to several treatments to separate two concentrate of cerium and light rare earth elements. These treatments include:

a- Conversion of the double sulfate concentrates to hydroxide by adding sodium hydroxide pellets equivalent to about 20% and finely agitated then left over night[13].

b- The resultant hydroxide slurries were then washed efficiently through re-pulping with water and decantation several times then filtered.

c- The hydroxide was then dried at 180°C for 10 hours where most of the cerous constituents converted to ceric.

d- Most of the trivalent rare earth elements were leached from ceric using l M HNO_3 under pH



Scheme 4 : Steps for preparation cerium and light rare earth concentrates

control of 3. Two cerium concentrates were produced containing also thorium and uranium.

e- The leached trivalent rare earth elements, composed mainly from light rare earth, were subjected to fractional precipitation using 10% sodium hydroxide. Three precipitates were prepared at different successive pH values of 7.5, 8.5 and 9.5.

The prepared concentrates were characterized X-ray Fluorescence Spectrometer, Bruker Pioneer S4.

RESULTS AND DISCUSSION

The Egyptian crude monazite sand assaying 47% monazite is generally having a size of about - 65 mesh. However, the high grade Egyptian monazite sand (97% monazite) contains more than 61.2% REE_2O_3, 27.8% P_2O_5, 5.8% ThO_2, 0.5% U_3O_8 and 4.7% others[14]. Distribution of the rare earth oxides in the Egyptian monazite are illustrated in TABLE 1. It is clear that the light rare earth oxides (LREO) (La, Ce, Pr, Nd, Sm) compose 93.3% of the total rare earth oxides while the heavy rare earth oxides (HREO) represent only 6.7%.

Digestion of crude monazite under the conditions of 93% H_2SO_4 acid initially heated to 180°C and in weight ratio to the monazite of 2.5 was added gradually then heated to 220°C for 2.5 hr. The digestion efficiency under these conditions is illustrated in TABLE 2.

The gray past product was cooled to room temperature then leached through two successive steps. The first leach solution of 220 l contains 9.1 g Ce/l and 4.5 g Th/l, while the second leach solution of 120 l contains 23.1 g Ce/l and 1.2 g Th/l. This means that about 60% of cerium and in consequence the other rare earth elements were dissolved during the second leaching.

Effect of anhydrous sodium sulfate on cerium precipitation

Cerium represents the major constituent of light rare earth in the monazite sand, so its precipitation with anhydrous sodium sulfate was studied at ambient temperature and mixing for 3 hours. Results of double sulfate precipitate are shown in TABLES 3 and 4. The results reveal that cerium concentration was decreased from 9.1 to 0.76 g/l with adding 40 g Na_2SO_4/l in the case of first leach solution. It was decreased from 23.1 to 0.9 g/l with adding 70 g Na_2SO_4/l in the case of second leach solution. However, more than half of the present thorium was co-precipitated in the case of first leach solution where its concentration was decreased from 4.5 to 2.1 g/l. In the case of second leach solution it was decreased from 1.2 to 0.36 g/l. This means that about 70% of the present thorium was co-precipitated.

The results of anhydrous sodium sulfate concentration on precipitation were applied upon the two leach solutions where 45 g/l and 70 g/l Na_2SO_4 was used for the 1st (220 l) and 2nd (120 l) solution, respectively. The precipitation efficiency of both cerium and thorium from these solutions is shown in TABLE 5. From these results it is clear that the precipitation efficiency for both cerium and thorium was 91.8% and 53.8% from the 1st leach solution where it was 96.0% and 70.3% from the 2nd leach solution, respectively.

TABLE 1 : Distribution of the rare earth oxides in the Egyptian monazite

HREO	Distribution, %
Eu_2O_3	0.7
Gd_2O_3	1.8
Dy_2O_3	0.8
Ho_2O_3	0.3
Er_2O_3	0.4
Tm_2O_3	0.3
Yb_2O_3	0.1
Y_2O_3	2.3
$\sum$	6.7%

LREO	Distribution, %
La_2O_3	23.2
Ce_2O_3	44.7
Pr_6O_{11}	4.7
Nd_2O_3	17.6
Sm_2O_3	3.1
$\sum$	93.3%

TABLE 2 : Digestion efficiency of cerium, thorium and the overall monazite

Element	digestion efficiency, %
Ce	91.2
Th	96.6
monazite sand	92.1

After converting the two sodium rare earth double sulfate precipitates to hydroxides, washing and drying at 180°C for 10 hours, their weights, quantitative chemical analysis of cerium and thorium are indicated in TABLE 6 while qualitative constituents of rare earth and other major elements are indicated in TABLE 7.

Composition of cerium concentrates

Analysis of the prepared cerium concentrates are shown in TABLE 8. The two cerium concentrates contained about 47, 48% CeO_2, 11, 13% other light rare earth elements and 3, 3.8% ThO_2.

TABLE 3 : Effect of the added anhydrous sodium sulfate on cerium and thorium precipitation from the 1st leach solution (2 hr, ambient temp.)

Equivalent Na_2SO_4 added, g/l	conc. after ppt^{tion} from the 1st leach solution, g/l	
	Ce (Org. conc. 9.1 g/l)	Th (Org. conc. 4.5 g/l)
10	1.6	2.8
20	0.93	2.5
30	0.82	2.2
40	0.76	2.1
45	0.75	2.1

TABLE 4 : Effect of the added anhydrous sodium precipitation from the 2nd leach solution (2 hr, ambient temp.)

Equivalent Na_2SO_4 added, g/l	conc. after ppt^{tion} from the 2nd leach solution, g/l	
	Ce (Org. conc. 23.1 g/l)	Th (Org. conc. 1.2 g/l)
30	3.2	0.64
40	1.9	0.58
50	1.3	0.5
60	1.1	0.44
70	0.9	0.36

TABLE 5 : Anhydrous sodium sulfate precipitation efficiency from the leach solutions

Element	precipitation efficiency from leach solution, %	
	1st	2nd
Ce	90.3	96.6
Th	42.6	70.3

TABLE 6 : Weight, cerium and thorium concentrations in the prepared two concentrates from double sulfate precipitation

	Precipitate from 1st leach solution	Precipitate from 2nd leach solution
Wt., Kg	5.74	7.95
Ce, %	31.35	33.74
Th,%	7.3	1.34

TABLE 7 : Composition of rare earth and other major elements in the prepared two concentrates from double surface precipitation using SEM

Element, %	Precipitate from 1st leach solution	Precipitate from 2nd leach solution
Ce	37.85	42.62
La	19.52	21.1
Nd	15.68	17.1
Pr	3.18	4.47
Sm	1.98	2.46
Eu	0.30	0.58
Gd	0.52	1.19
∑ REE	78.21	89.52
Th	11.95	2.51
U	1.56	0.58
Ca	4.20	0.99
S	1.15	1.58
P	0.95	0.57
Si	0.70	1.01
Al	0.56	0.74

TABLE 8 : Composition of cerium, light rare earth and the other elements in the two prepared cerium concentrates

Oxide, %	Ceric oxide 1	Ceric oxide 2
CeO_2	48.11	47.3
La_2O_3	4.99	4.05
Nd_2O_3	5.33	5.11
Pr_6O_{11}	1.70	1.49
Sm_2O_3	1.10	---
∑ LREE	13.12	10.65
ThO_2	3.01	3.77
UO_2	0.03	0.04
Na_2O	4.36	8.79
CaO	0.18	0.47
MgO	----	0.09
Fe_2O_3	0.15	---

The other rare earth elements concentration, if present, is less than 0.3%

Composition of the concentrates after cerium separation

Results of analysis the three concentrates prepared after fractional precipitation from the leach solutions containing trivalent rare earth elements at different pH values are shown in TABLE 9.

The major concentrate was precipitated at pH 7.5 and represents more than 93% of the total three concentrates weight. This concentrate composed mainly of light rare earth elements (more than 64% La, Nd, Pr and Sm oxides) with only 5.7% Ce oxide and 2.3% of Gd oxide. The concentrate precipitated at pH 8.5 represents only 1.3% of the total three concentrates weight and containing 7.5% oxides of the light rare earth from which 0.6% Ce oxide. The later concentrate precipitated at pH 9.5 represents 5.5% of the total three concentrates and containing less than 1% of the light rare earth oxides. Accordingly, it would be recommended to precipitate the trivalent light rare earth elements at pH 8.5.

Analysis of the prepared oxalate heavy rare earth concentrates (1) and (2) is shown in TABLE 10.

Results reveal that the first oxalate heavy rare earth concentrate are composed mainly from yttrium (about 18% Y_2O_3) while containing about 1.4 and 2.5% of both Gd_2O_3 and Dy_2O_3 respectively. The second oxalate concentrate contained high thorium (about 14% ThO_2), cerium (more than 17% CeO_2) and light rare earth element oxides (about 22%) while the heavy rare earth element oxides content were only about 11%. The third concentrate prepared at pH 3.6 (TABLE 11) composed mainly of iron (more than 22%) and containing 4%, 6.5% and 7% of cerium, yttrium and uranium, respectively. The fourth concentrate prepared at pH 7.5 (TABLE 11) composed of 5.5% uranium, 5.8% iron and 3.6% chromium.

CONCLUSION AND RECOMMENDATIONS

It may be beneficial to prepare concentrates of cerium, light and heavy rare earth elements in early

TABLE 9 : Composition of the light rare earth elements in prepared three concentrates 3.4. composition of the heavy rare earth oxalate concentrates

Oxide, %	concentrates prepared at pH		
	7.5	8.5	9.5
La_2O_3	28.6	4.95	0.55
Nd_2O_3	25.89	1.6	0.37
Pr_6O_{11}	5.74	0.37	0.06
CeO_2	5.47	0.64	0.06
Sm_2O_3	4.18	0.15	0.05
$\sum$ LREE	69.88	7.71	1.09
Gd_2O_3	2.04	0.08	----
Dy_2O_3	0.33	----	----
Y_2O_3	0.90	0.04	---
$\sum$ HREE	3.27	0.12	----
ThO_2	----	0.04	----
UO_2	0.14	----	----
Na_2O	----	3.04	0.53
CaO	1.38	48.8	59.3
MgO	0.52	17.8	11.6
Fe_2O_3	----	0.05	0.03

The other rare earth elements concentration, if present, is less than 0.3%

TABLE 10 : Composition of the two prepared rare earth oxalate concentrates (1) and (2)

Oxide, %	prepared concentrates	
	Oxalate 1	Oxalate 2
Y_2O_3	17.8	6.36
Gd_2O_3	1.39	2.66
Dy_2O_3	2.69	1.55
Ho_2O_3	----	0.32
Tb_2O_3	0.31	0.31
Er_2O_3	----	0.02
$\sum$ HREE	22.19	11.22
CeO_2	0.13	17.3
La_2O_3	0.47	10.5
Nd_2O_3	0.19	8.02
Pr_6O_{11}	----	1.78
Sm_2O_3	----	1.65
$\sum$ LREE	0.79	39.25
ThO_2	----	13.9
Na_2O	11.8	7.02
CaO	1.46	1.69
Fe_2O_3	0.04	0.33

TABLE 11 : Composition of the third and fourth concentrates prepared at pH 3.6 and pH 7.5 using Scanning electron microscope (ESEM)

Element, %	prepared concentrates	
	Oxalate 3	Oxalate 4
C	5.94	6.72
O	29.47	34.5
Na	6.46	26.07
Mg	-----	0.40
Si	-----	0.21
P	11.37	7.20
S	-----	3.54
Cl	-----	5.26
Ca	4.78	1.33
Ti	1.69	-----
Ce	4.08	-----
Cr	-----	3.55
Fe	22.66	5.77
U	7.08	5.47
Y	6.46	-----

stage to facilitate the subsequent separation of each element in high grade as well as for economical considerations. In this regard, the Egyptian crude monazite sand was treated to firstly separate most of thorium with part of rare earth elements in first leaching step, while the remaining rare earth elements would be completely leached in second step. Rare earth elements could be fractionated using selective precipitation of most light rare earth elements as sodium light rare earth double sulfate, from which cerium could be easily separated depending upon change its oxidation state from Ce^{3+} to Ce^{4+}. The other trivalent light rare earth elements leached from Ce^{4+} could be precipitated at pH 8.5 to form concentrate of them. It is worthy to mention that, thorium was co-precipitated with the double sulfate and oxalate, so it should be pre-precipitated before performing either of the mentioned selective precipitation routes.

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